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EUTECTIC BONDING OF A TI SPUTTER COATED, CARBON AEROGEL WAFER TO A NI FOIL

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The formation of high energy density, storage devices is achievable using composite material systems. Alternate layering of carbon aerogel wafers and Ni foils with microporous separators is a prospective composite for capacitor applications. An inherent problem exists to form a physical bond between Ni and the porous carbon wafer. The bonding process must be limited to temperatures less than 1000°C, at which point the aerogel begins to degrade. The advantage of a low temperature eutectic in the Ni-Ti alloy system solves this problem. Ti, a carbide former, is readily adherent as a sputter deposited thin film onto the carbon wafer. A vacuum bonding process is then used to join the Ni foil and Ti coating through eutectic phase formation. The parameters required for successful bonding are described along with a structural characterization of the Ni foil-carbon aerogel wafer interface.

1. INTRODUCTION

The nanometric size pores characteristic of aerogel materials leads to corresponding physical features of high porosity, a large surface area to mass ratio, and low density. For example, a bulk density of a carbon aerogel less than 0.1 $g\,cm^{-3}$ is routinely attainable. The high porosity of aerogel materials makes them excellent thermal insulators with conductivities ($\sim 10^{-2}$ $W\,m^{-1}\,K^{-1}$) two orders of magnitude below the equivalent fully dense solid. Recent investigation of the electrical conductivity (~ 1 $\Omega^{-1}\,cm^{-1}$) of monolithic carbon aerogels[1] has lead to the potential application of carbon aerogel wafers in energy storage devices[2].

A prototype for a high ouput, energy storage device is an electrochemical double layer capacitor (EDLC).[2] Since capacitance is proportional to surface area, only electrochemically inert materials of the highest specific surface area can be used to make rechargeable EDLCs. Aerogel wafers have large surface areas ($\sim 10^2$ $m^2\,cm^{-3}$) which account for demonstrated capacitances of 35 $F\,cm^{-3}$ and small bulk densities (<1 $g\,cm^{-3}$) that permit stored energy to be rapidly released yielding high power densities. An EDLC which consists of carbon aerogel layers (used for the battery electrodes) separated by an electrolyte wetted microporous glass can yield power densities greater than 5 $kW\,kg^{-1}$. Ni mesh or foil serves as a low resistance contact to the power cell. Power densities can be increased by decreasing the thickness of the aerogel and microporous separator. Among the factors which can further improve performance is the reduction of internal resistance. This can be accomplished, for example, by improving the surface contact at the Ni-aerogel interface.[3]

To fabricate a capacitor, a bonding scheme must be devised to join the contact layer (as the Ni foil) to the carbon aerogel wafer. The productive use of conductive epoxies as an effective joining medium has met with limited success since bond failure can be prevalent during temperature cycling in service. In this study, a bonding procedure is developed between a Ni foil and carbon aerogel wafer without the use of conductive epoxies. A metallic bond is formed between the Ni foil and carbon aerogel wafer through the use of a intermediate metallization layer. Ti is selected as the material for the thin film coating on the carbon aerogel wafer since is forms both a low temperature eutectic[4] with Ni at 942 °C (below the 1050 °C degradation temperature of the aerogel wafer) and readily wets C (as Ti is a carbide former). The coating and bonding processes will be described and characterized in this paper.

2. EXPERIMENTAL METHOD

The sputter deposition process used to coat the carbon aerogel wafer with Ti and the vacuum bonding procedure will be reviewed, whereas the detailed procedure used to synthesize organic aerogels can be found elsewhere[5]. In brief, carbon aereogels are derived from organic aerogels which are formed via aqeous polycondensation of resorcinol with formaldehyde. The resorcinol-formaldehyde (RF) clusters cross-link to form a gel that is exchanged with an organic solvent and then liquid CO_2. The RF aerogels are pyrolized in N_2 at 1050 °C. Wafers with a density of 0.80 g cm^{-3} are cut to a thickness of 0.28 mm (11 mils) from a cylindrical monolithe.[2]

The deposition process is conducted in a vacuum chamber cryogenically pumped to a base pressure of 0.05 µTorr. A high purity (>0.9994) titanium target is sputtered with a planar magnetron using a working gas of high purity Ar at a pressure of 5.0 mTorr and a flow of 20 cc min^{-1}. A discharge voltage of 370 V at a current of 0.80 amps produces a Ti deposition rate of 1.4 nm s^{-1}. The stationary, aerogel substrate is situated 10 cm from the surface of the transverse mounted magnetron sources. A selection of a 1 and 4 µm thickness for the titanium coating is made in order to provide complete surface coverage at a thickness which exceeds the height of the topological surface wave attributable to the wafer finish. Contact profilometry is used to measure the coating thickness.

A 25μm (1 mil) thick Ni foil is bonded to 1cm x 2cm strips of Ti coated, carbon aerogel wafers in a vacuum furnace. A quartz tube is heated using a Lindberg furnace after being turbomolecularly pumped to a base pressure of 0.10 μTorr. The vacuum pressure in the quartz tube does not exceed 1 μTorr as the first three samples are heated from room temperature to 950 °C at a rate <10 °C min^{-1}, held at temperature for 15 min, then cooled down at a rate <20 °C min^{-1} to room temperature. The three samples consist of gravity loaded (at 27 gm cm^{-2}) Ni foil in contact with (1) an uncoated wafer; (2) an aerogel wafer with 1μm Ti coating; and (3) an aerogel wafer with 4μm Ti coating. An additonal bonding experiment (4) is performed between the 4μm Ti coated aerogel wafer and the Ni foil for an extended time of 30 min at 950 °C. The bond is fractured by pulling the Ni foil from the Ti coated, aerogel wafer to failure.

Primary characterization of the coatings and fracture surfaces is accomplished using scanning electron microscopy (SEM). Back-scattered electron imaging facilitates differentiation of surface composition whereas secondary electron imaging reveals details of the surface morphology. The texture of the as-deposited coatings are determined with a conventional powder diffractometer operated in the θ/2θ mode using monochromatic Cu $K\alpha$ x-rays.

3. RESULTS AND ANALYSIS

The Ti coatings are specular, highly textured along [00.2], and adherent to the carbon aerogel wafers. The actual Ti coating thicknesses are measured at 1.0 and 3.7 μm using contact profilometry. The aerogel surface is featureless providing a smooth surface for the Ti coatings (Fig. 1a). The 1.0 and 3.7μm Ti coatings have a dense columnar morphology typical for low temperature sputter deposits along with 30 and 45 nm grain size, respectively (Figs. 1b,c). After the vacuum bonding process the Ni foil is pulled from the aerogel wafer. The formation of Ti-carbides is not anticipated or subsequently evidenced in x-ray diffraction scans since the vacuum bonding process temperature is below the degradation temperature of the pyrolitic carbon and noting that the Ti_2C eutectic temperature is 1648 °C as taken from the Ti-C phase diagram.[4] The exposed fracture surfaces are characterized with SEM imaging to identify the mode of interface failure. The extent of bonding between the Ni foil and Ti coated substrate is given by a surface area (%) measurement of aerogel matrix pullout found on the Ni foil. The characterization results for each bonding experiment are summarized as follows. (1) No indication of any adhesion exists between the uncoated aerogel wafer and the Ni foil. (2) Local adhesion of the Ni foil is observed with polygons of carbon pullout that occupy ~5% of the surface area (Fig. 2). Typical sizes are no greater than 0.5mm x 1mm. (3) Local adhesion of the Ni foil is observed with polygons of carbon pullout (as large as 1mm x 3mm in size) that occupy ~28% of the surface area (Fig. 3a). After bonding, the Ti film is recystallized to equiaxed grains from its original columnar shape (Fig. 3b). The Ti coating remains adherent to the carbon wafer without any apparent Ti-C interdiffusion or intermetallic formation. Localized fracture of the Ni-Ti bond is evident at the edges of the carbon pullout. Thermal grooving of the Ni grain boundaries is also evident on the foil surface. (4) Local adhesion of the Ni foil is observed with polygons of carbon pullout (as large as 2mm x 3mm in size) that occupy >34% of the surface area (Fig. 4). Many of the aerogel pullout polygons have a rectangular-like shape. The long axis of these polygons is concident with the direction the Ni foil is pulled from the aerogel wafer.

An attempt to enhance the surface wetting of the Ti coated wafer with the Ni foil during bonding was made by overcoating the 3.7μm Ti layer with a submicron Ni layer. Residual stresses introduced by the Ni overcoat layer induced delamination of the Ti coating from ther aerogel wafer prior to the vacuum bonding procedure.

4. DISCUSSION & SUMMARY

A thicker Ti coating (3.7 μm compared to 1 μm) proved advantageous to promote surface contact, hence bonding of the Ni foil to the Ti coated aerogel wafer. No attempt was made to increase the surface contact between the Ni foil and aerogel wafer prior to vacuum bonding (e.g. by rolling) other than through static loading since the carbon wafers are rigid and brittle. The increase of time at temperature (above the Ni-Ti eutectic) during the vacuum bonding process promoted an increase in the surface area of adhesion between the Ni foil and coated aerogel wafer. This result naturally occurs since the additional time provides for further conforming of the Ni foil to the Ti coated wafer (hence wetting) at the forming Ni-Ti interface.

ACKNOWLEDGMENTS

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Figure Captions

1 The secondary electron images of the surface of the (a) uncoated carbon aerogel wafer, (b) the 1.0μm thick Ti coating and (c) the 3.7 μm thick Ti coating.

2 A secondary electron image of the fracture surface of the 1.0μm thick Ti coated aerogel wafer subsequent to the 950°C-15min bonding procedure.

3 Secondary electron images of the Ni foil after fracture surface after from the 3.7μm thick Ti coated aerogel wafer subsequent to the 950°C-15min bonding procedure as viewed (a) at 60° off the surface normal and (b) along the Ni-Ti-C wafer interface.

4 A secondary electron image of the Ni foil surface after fracture from the 3.7μm thick Ti coated aerogel wafer subsequent to the 950°C-30min bonding procedure.

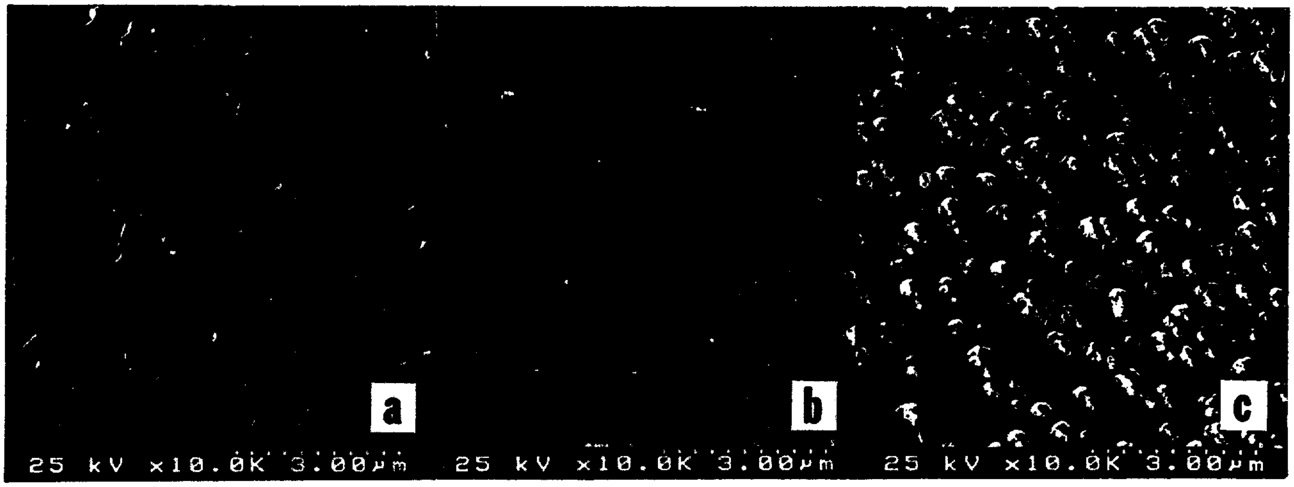

Figure 1.

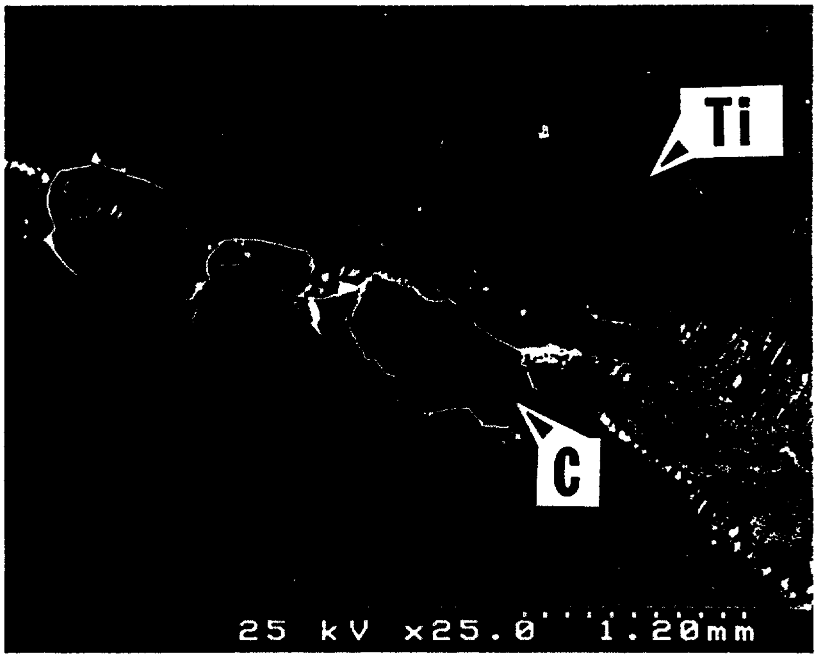

Figure 2.

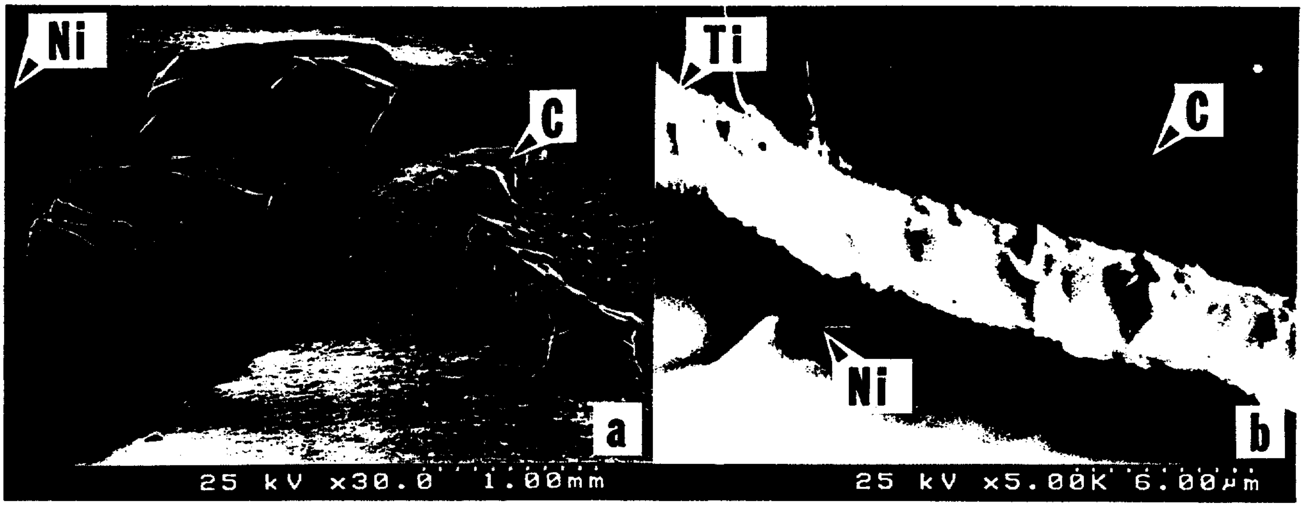

Figure 3.

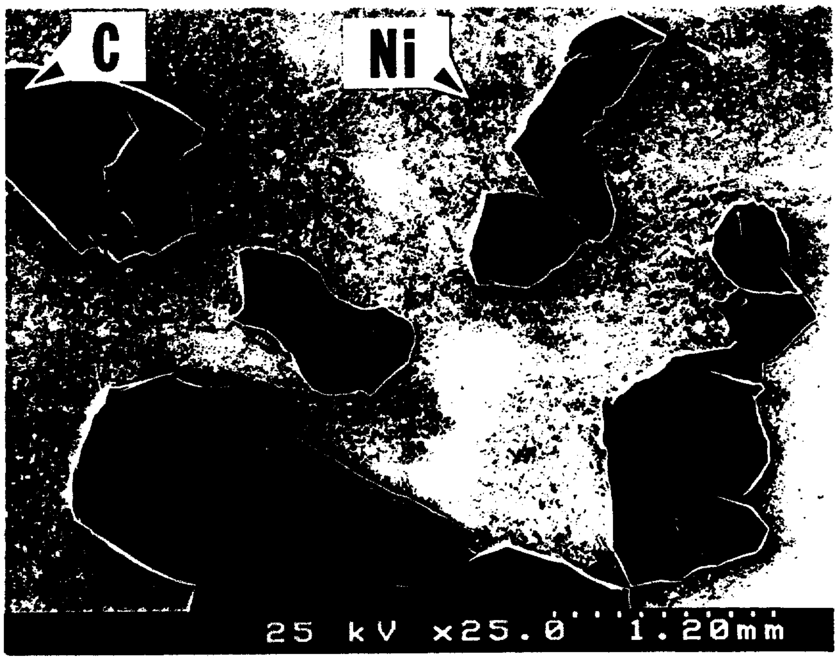

Figure 4.

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